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XVIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON BENZOLTRISULPHONIC ACID.

By C. Loring Jackson and John F. Wing.

Presented March 9, 1887.

The benzoltrisulphonic acid has been prepared up to this time only by Senhofer,* who made it by heating a mixture of benzol, fuming sulphuric acid, and phosphoric pentoxide to 280°–290° in a sealed tube, and studied its potassium, barium, lead, and silver salts, while in a subsequent paper † he made a thorough investigation of the action of melted potassic hydrate upon it, — a large amount of work when the extreme difficulty of the method of preparation is considered.

Our attention was first drawn to this substance while we were trying to make the potassic benzolparadisulphonate by the method of Barth and Senhofer,‡ and encountered in one preparation large well-formed crystals, giving with phosphoric pentachloride a chloride melting above 180°, which proved on analysis to be Senhofer's potassic benzoltrisulphonate. As we could find no mention of the appearance of the trisulphonate under these conditions in the papers of Barth and Senhofer,‡ Koerner and Monselise,§ or of any other chemists who have studied the action of sulphuric acid on benzol, we searched for the cause of this abnormal result, and soon found it in the fact that we had heated the crude potassic disulphonate a second time with fuming sulphuric acid. After this a few experiments were enough to prove that the action was due to the presence of potassic sulphate, and, to our great surprise, that common sulphuric acid in presence of potassic sulphate was capable of converting a benzolsulphonic acid into the trisulphonic acid, and was as efficient in this respect as the fuming sulphuric acid.

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* Ann. Chem., clxxiv. 243.

† Wien. Acad. Ber., Ser. 2, lxxviii. 677.

‡ Ber. d. ch. G., 1875, p. 1478.

§ Gazz. Chim., 1876, p. 133.

This result, it seems to us, throws light on the beautiful method of preparing trisulphonic acids, the application of which to toluol was published by Claësson* in 1881, and which consists in heating a potassic sulphonate with chlorsulphonic acid, since it makes it probable that the reaction is due to the acid potassic sulphate formed during the process, rather than to the chlorsulphonic acid itself. In a general way also our process resembles that of Neville and Winther † for converting the amido compounds into their monosulphonic acids by the action of heat on their acid sulphates, although it is doubtful whether the mode of action of the two processes is the same, since in ours the presence of an excess of sulphuric acid is essential.

As our process converts the benzoltrisulphonic acid from one of the least into one of the most accessible of the less common aromatic compounds, we have devoted some time to its study, and in this paper, after giving the details of our preliminary experiments, and the methods for preparing the benzoltrisulphonic acid, we describe the first results that we have obtained; which consist of the determination of the crystalline form and solubility of the potassium salt, ‡ the preparation and study of the chloride, the ester, which exhibits a strange instability, the amide with several of its metallic derivatives, and its benzoyl compound, and as this, like the corresponding compound of the benzolmonosulphamide is an acid, its sodium and barium salts and chloride with the phenylamidine derived from it, the anilid, and finally the proof by two different methods that the benzoltrisulphonic acid has the symmetrical constitution 1, 3, 5.

Formation of Benzoltrisulphonic Acid.

To prove that the presence of potassic sulphate was the cause of the formation of the trisulphonic acid, a solution of benzol in fuming sulphuric acid, to which its own volume of common sulphuric acid had been added, was divided into two equal parts, (*a*) and (*b*), and, after adding a quantity of potassic sulphate to (*a*), both parts were heated in retorts under precisely the same conditions until half of the liquid had passed over. The residues were converted into potassium salts, and recrystallized, when (*a*) furnished the very characteristic crystals of the potassic benzoltrisulphonate, and gave a chloride which, after washing with ether and one crystallization from chloroform, melted at

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* Ber. d. ch. G., 1881, p. 307.

† Ibid., 1880, p. 1940.

‡ Also some attempts to prepare substituted trisulphonic acids, which led to negative results.

182° ($C_6H_3(SO_2Cl)_3$ melts at 184°), proving that the trisulphonic acid had been formed, while (*b*) gave a potassium salt crystallizing in an asbestos-like* mass, which yielded a viscous chloride, from which no trace of the benzoltrisulphochloride could be obtained; and, as both the potassic benzoltrisulphonate and its chloride are very characteristic substances, there can be no doubt that in this latter case no appreciable amount of the trisulphonic acid was formed. In a second experiment the benzolmetadisulphonic acid (made by heating the chloride with water to 150° in a sealed tube) was used, and the result was the same; the specimen heated with sulphuric acid and potassic sulphate gave benzoltrisulphonic acid recognized as in the previous experiment, while that heated with sulphuric acid alone gave no trace of this product.

The experiments just described having proved that the presence of potassic sulphate is necessary for the formation of the trisulphonic acid, we next considered the question, "Cannot the trisulphonic acid be formed by the action of acid potassic sulphate alone without an excess of sulphuric acid?" and found that potassic benzolmetadisulphonate fused with acid potassic sulphate remained unaltered, even at a temperature where the mass began to char. It is evident, therefore, that the potassic sulphate serves only to render the sulphuric acid more efficient, and it remained to determine by experiment, if possible, the manner of its action. Since in Senhofer's method, the only one beside ours by which the benzoltrisulphonic acid has been obtained, the action was due to the presence of a powerful dehydrating agent (phosphoric pentoxide), the most plausible theory was that the acid potassic sulphate acted simply by the removal of water. To test this hypothesis we substituted for the potassic sulphate in one experiment argentic sulphate, and in another zincic sulphate, as, if the action of the salt is due only to its attraction for water, like that of the phosphoric pentoxide in Senhofer's method, the latter should produce quite as good a result as potassic sulphate, whereas the argentic sulphate would be entirely without action. Upon heating three portions of benzolmetadisulphonic acid with the same proportion of sulphuric acid, (*a*) without the addition of a salt, (*b*) with addition of zincic sulphate, and (*c*) with addition of argentic sulphate, we found that, while no trace of the trisulphonic acid could be detected in (*a*), or (*b*), it was formed in large quantity in (*c*), and, if anything, was accompanied with less of the tarry secondary products than when potassic sulphate was used, so that argentic sulphate could perhaps be used advantageously in place of potassic sulphate in the manufacture of the trisulphonic acid, since, owing to its slight solubility, it can be filtered out with little loss after the addition of water to the product of the reaction, and is then ready to use again after drying. It follows from the above results that the salt does not act as a dehydrating agent, but rather as a carrier of the sulphuric acid, owing to the formation of an acid salt.

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* We have not succeeded in determining the nature of this potassium salt. It does not resemble the potassic benzolmonosulphonate, which crystallizes in glistening plates, nor have we found any disulphonate corresponding to it in properties. We hope to return to this subject hereafter.

The experiments just described have led us to the following hypothesis to explain the formation of the benzoltrisulphonate by the action of potassic sulphate and sulphuric acid; but we wish it distinctly understood that we could find no way of submitting this hypothesis to a complete experimental proof, and therefore offer it simply as the most plausible explanation of the observed facts that we have been able to find. The acid potassic sulphate formed by the sulphuric acid and potassic sulphate is first, we suppose, converted into the potassic pyrosulphate by loss of water, and the pyrosulphate in its turn decomposed by the sulphuric acid, giving potassic sulphate and fuming sulphuric acid, which, breaking up into H_2SO_4 and SO_3, furnishes the nascent sulphuric anhydride to form the benzoltrisulphonic acid, while the potassic sulphate goes through the same series of reactions again, which can be written as follows: —

$$K_2SO_4 + H_2SO_4 = 2\ KHSO_4$$

$$2\ KHSO_4 = K_2S_2O_7 + H_2O$$

$$K_2S_2O_7 + H_2SO_4 = K_2SO_4 + H_2S_2O_7 = K_2SO_4 + H_2SO_4 + SO_3.$$

Of these reactions the second can be considered well established, since the proportion of acid to potassic sulphate in the mixture used by us is almost exactly one molecule of K_2SO_4 to two of H_2SO_4; and it has been found,* when such a solution is allowed to cool, that it deposits first the neutral salt K_2SO_4, and afterward the potassic pyrosulphate $K_2S_2O_7$. But the last reaction is certainly not above criticism, since in it sulphuric acid is made to displace pyrosulphuric acid, which last, it is fair to suppose, is the stronger of the two. In answer to this we would suggest, that the reaction either may be brought under Berthollet's law on account of the formation of the volatile sulphuric anhydride, or, what seems to us more probable, it is brought about by the concurrent attraction of the sulphuric anhydride for the benzoldisulphonic acid. It is possible, however, that one of the two following reactions may express the action more correctly, —

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* Gmelin Kraut., 1875, ii. 48.

$$KHSO_4 + C_6H_4(SO_3H)_2 = C_6H_3(SO_3H)_2SO_3K + H_2O.$$

$$K_2S_2O_7 + 2\ C_6H_4(SO_3H)_2 = 2\ C_6H_3(SO_3H)_2SO_3K + H_2O.$$

But in these reactions the excess of sulphuric acid must be supposed to act as a dehydrating agent, and thus produce the action, since we have proved experimentally that no action takes place when an excess of sulphuric acid is absent; and this observation seems to us to make these two reactions less probable than the series in which sulphuric anhydride is formed.

We have not multiplied experiments with different metallic sulphates, as it has not seemed to us that such work would throw any additional light on the theory of the process; we may mention, however, that we have also tried aluminic sulphate, which gave rise to the formation of a little trisulphonate when heated with metadisulphonic acid and sulphuric acid, but, as far as we could judge, was much less efficient in its action than the potassic sulphate.

Preparation of Benzoltrisulphonic Acid.

As the result of many experiments we have worked out the following process for preparing benzoltrisulphonic acid from potassic benzolmetadisulphonate, — 15 grams of potassic benzolmetadisulphonate, which need not be freed from its water of crystallization, are mixed in a porcelain dish with 18 grams of common strong sulphuric acid,* and heated with the free flame, care being taken to avoid heating the edges of the liquid too intensely during the first stage of the process, as at this time there is danger of charring. After the salt has dissolved, the sulphuric acid begins to come off in heavy white fumes, but without the formation of bubbles; in fact, there is no bumping or tumultuous evolution of vapor in any part of the process. If the operation is stopped at this point, the disulphonate will be found unaltered. After heating for a few minutes, little bubbles appear in large numbers, and soon after the mass becomes pasty, and begins to puff up, while the evolution of fumes slackens; at this point the lamp is to be removed. The product, if charring was avoided in the early part of the process (there is little danger of it later), is of a reddish brown color, and almost completely solid. The loss in weight should be about 7 grams, and the whole operation takes little more than fifteen minutes. After the residue is cold, it is dissolved in water, and treated with an excess of baric carbonate to remove sulphuric acid, when the greater part of the colored impurity is carried down by the baric sulphate, so that the filtrate is usually of a pale wine-yellow. The precipitate should be boiled out with water once or twice, and the washings added to the filtrate, which, after converting any barium salt into potassic trisulphonate by potassic sulphate, is evaporated until its surface after cooling is covered with little crystals, when it usually deposits fine crystals after a short time, which can be increased in size by the spontaneous evaporation of part of the mother liquor, and purified by recrystallization from boiling water. The mother liquors, when sufficiently concentrated, solidify to a brownish pasty mass of a finely granular consistency, filled with larger crystals of potassic benzoltrisulphonate, which can be separated mechanically by scraping with a flat-pointed platinum stirrer the semi-liquid finer-grained impurity through the holes in a perforated platinum cone placed in a funnel. The larger crystals left behind are then purified by crystallization from water. The yield from this process can be raised by careful work to 44 per cent of the theoretical yield, and it is possible to increase it still further by boiling the precipitate formed by baric carbonate with a solution of potassic carbonate, as the baric benzoltrisulphonate is very sparingly soluble in water. We cannot recommend this treatment, however, as the potassic benzoltrisulphonate extracted in this way is contaminated to such an extent with the colored impurities carried down by the precipitate of barium salts, that it is very hard to obtain white and pure crystals from it; in fact, it is easier to prepare fresh from the benzolmetadisulphonate.

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* Double these quantities can be used, but it is not convenient to work with much larger quantities than 30 grams at a time. The benzolmetadisulphonate may contain a small quantity of potassic carbonate or sulphate without injury to the process, but should be free from colored tarry impurities.

The benzoltrisulphonic acid can also be prepared from benzol without isolating the lower sulphonic acids, and this method is sometimes convenient when large quantities of the substance are desired; but it is decidedly inferior to that just described, for two reasons, first, because the yield is very much smaller, and, second, a certain amount of benzolparadisulphonate is formed, which it is not easy to separate from the trisulphonate by crystallization. For this purpose 100 (or more) grams of benzol are dissolved in the same volume of common sulphuric acid by boiling them together in a flask with a reverse cooler;* when the solution is complete, the product is mixed with its own volume of common sulphuric acid and between 60 and 70 grams of potassic sulphate, and distilled in an untubulated retort till about one third of the total amount of sulphuric acid used has passed over. The liquid boils quietly without bumping. The residue is then divided into two parts, and these are heated in porcelain dishes precisely as in the previous process. The product is much more impure than when made from the potassic disulphonate, and it is better therefore to decolorize it by treatment with plumbic oxide after a part, but not the whole, of the large excess of sulphuric acid has been removed by marble or baric carbonate, since the greater part of the coloring matter is precipitated on adding an excess of plumbic oxide if the solution is acid, and still more comes down with the plumbic carbonate when potassic carbonate is added to the filtrate; but if the solution is thoroughly neutralized by the marble, very little, if any, of the colored impurity comes down with the lead salts, and in that case it is very hard to get rid of it. The yield was very small, and, although we could have raised it undoubtedly by working up the insoluble residues, we have never tried to do so, because we have found it easier to prepare a fresh portion than to purify the highly colored salts which would be obtained in this way. It is advisable, however, to heat once more with sulphuric acid the brown impure residues left by the evaporation of the mother liquors, from which no more crystals of benzoltrisulphonate can be separated, as in this way an additional quantity of the trisulphonate can be obtained. We have tried also to purify the impure residues left after the removal of the crystals by treatment with phosphoric pentachloride, and washing the product with ether or chloroform, but have obtained only unsatisfactory results.

The secondary products formed in this process are of little or no interest. They consist principally of a dark reddish brown to black substance giving a potassium salt of tarry consistency more soluble than the potassic benzoltrisulphonate, which it will not be easy to purify. There appears also on evaporation of the mother liquors a dark-colored granular potassium salt, whose viscous chloride solidifies after standing for some weeks, and it is then possible to obtain much benzoltrisulphochloride from it by treatment with chloroform; it is probable, therefore, that it consists principally of the benzoltrisulphonate prevented from crystallizing by the presence of the dark-colored impurity just mentioned, or of some potassic benzolmetadisulphonate.

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* Michael and Adair, Ber. d. ch. G., 1877, p. 585.

If the trisulphonic acid was made direct from the monosulphonic acid, some benzolparadisulphonic acid was also formed, which made the purification of the benzoltrisulphonate by crystallization more difficult. It was recognized by the melting point of its chloride, 139°, whereas Koerner and Monselise* give 131°, and the following analysis of the chloride dried at 100°.

0.1008 grm. of substance gave after decomposition by boiling with a solution of pure sodic carbonate 0.1054 grm. of argentic chloride.

	Calculated for $C_6H_4(SO_2Cl)_2$.	Found.
Chlorine	25.82	25.86

We are inclined to consider the melting point (139°) given by us for the benzolparadisulphochloride as more accurate than that of Koerner and Monselise (131°), since their product was prepared from a mixture of the para and meta compounds, and a small quantity of the latter, melting at 63°, would have been enough to lower the melting point very considerably, and its presence could not be determined by analysis; the impurity in our product, on the other hand, would have been benzoltrisulphochloride, and that there could have been no appreciable amount of this substance present is shown conclusively by our analysis.

Benzoltrisulphonic Acid and its Salts.

We have little to add under this head to the excellent work of Senhofer. The free acid, when heated, became charred, and gave off a smell like caramel; but the soluble part of the residue consisted of the unaltered acid, as was shown by the crystalline form of its potassium salt and the melting point of its chloride. The experiment gave so little promise of interesting results, that it was not repeated on a larger scale. The following analysis of the free acid dried at 100°, which it was necessary to make in the course of our work, confirms Senhofer's statement that it retains three molecules of water at that temperature.

0.3772 grm. of the acid dried at 100° gave by the method of Carius 0.7004 grm. of baric sulphate.

	Calculated for $C_6H_3(SO_3H)_3\,3\,H_2O$.	Found.
Sulphur	25.80	25.51

We add also an analysis of the potassium salt, which yielded the same amount of water of crystallization (three molecules) as given by

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* Gazz. Chim., 1876, p. 140.

Senhofer; but, whereas he states that only one and a half molecules of the water are given off at 100°, we found that the whole was evolved at this temperature.

0.3768 grm. of air-dried salt at 100° lost 0.0431 grm.

	Calculated for $C_6H_3(SO_3K)_3$ 3 H_2O.	Found.
Water	11.11	11.43

0.7404 grm. of dry salt gave 0.442 grm. of potassic sulphate.

	Calculated for $C_6H_3(SO_3K)_3$.	Found.
Potassium	27.13	26.80

We have determined the solubility of the potassium salt as follows: —

I. 3.6594 grm. of a solution of $C_6H_3(SO_3K)_3$ saturated at 20° left on evaporation 1.3074 grm. of the salt dried at 260°.
II. 2.034 grm. of the solution gave 0.716 grm. of the dried salt.

Therefore a saturated solution of potassic benzoltrisulphonate at 20° contains the following percentages of the salt free from water of crystallization.

I.	II.
35.72	35.21

Dr. O. W. Huntington has at our request determined the crystalline form of the potassium salt $C_6H_3(SO_3K)_3$ 3 H_2O, and kindly furnishes us with the following statement: —

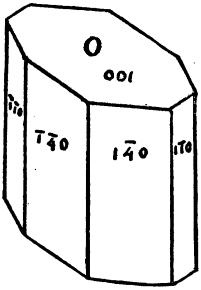

Fig. 1.

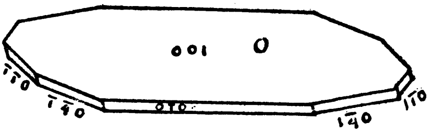

Fig. 2.

"Monoclinic, with marked variation of type. As no planes were observed except the basal plane and vertical domes, and pinacoids, it was impossible to make a complete determination of the crystal. The following measurements were obtained: —

$$001 \wedge 1\bar{1}0 = \mathbf{65^\circ\ 28'}$$
$$1\bar{1}0 \wedge 110 = \mathbf{50^\circ\ 55'}$$
$$1\bar{1}0 \wedge 1\bar{4}0 = 24^\circ\ 40'$$
$$1\bar{4}0 \wedge \bar{1}\bar{4}0 = 79^\circ\ 45'$$

Most of the faces of the crystals were uneven, and the angles printed in heavy type are the only ones which could be measured with accuracy.

"From these angles the inclination of the axes and the ratio of the ortho diagonal to the clino axis may easily be calculated.

$$\beta = 68^\circ\ 38'\ 30'' \qquad\qquad a : b = 1 : 2.10.$$

The crystals vary between the form shown in Fig. 1 and that of Fig. 2. In the second form the clino pinacoid is a characteristic feature which is absent in crystals of the first type, and the forms of both types run out into needles, in one case parallel to the vertical axis, and in the other parallel to the clino diagonal."

The potassium salt is not acted on by a cold solution of potassic permanganate, but, if heated with it, is oxidized, and we were unable to find any organic matter in the product.

The following attempts were made to obtain substituted benzoltrisulphonic acids. The silver salt was made by boiling the chloride with argentic oxide and water, and to the filtered solution bromine was added in order to make brombenzoltrisulphonic acid by the method of Nölting and Plawski,* which has been proved to be of wide application to monosulphonic acids by Limpricht.† A heavy precipitate of argentic bromide was formed at once, but the filtrate after being freed from compounds of bromine by evaporation gave a chloride melting at 184°, the melting point of benzoltrisulphochloride. It was analyzed also, as it was barely possible that the brombenzoltrisulphochloride might melt at the same temperature as the non-substituted compound.

0.2374 grm. of the substance gave 0.2718 grm. of argentic chloride.

	Calculated for $C_6H_3(SO_2Cl)_3$.	Found.
Chlorine	28.52	28.32

The argentic benzoltrisulphonate, therefore, is affected by bromine in an entirely different way from the monosulphonates. The filtrate before evaporation contained bromic acid, as was proved by the following experiments. Some of the filtrate containing no free bromine gave no precipitate when argentic nitrate was added, but upon boiling with alcohol a heavy precipitate of argentic bromide was formed; to another portion of this filtrate potassic iodide was added, when iodine was set free in large amount. The reaction must run as follows: —

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* Ber. d. ch. G., 1875, p. 819.

† Ann. Chem., clxxxvi. 134.

$$C_6H_3(SO_3Ag)_3 + 3\,Br_2 + 3\,H_2O = 3\,AgBr + C_6H_3(SO_3H)_3 + HBrO_3 + 2\,HBr.$$

Iodine acts on the argentic benzoltrisulphonate in a similar way. We have tried also to obtain a bromine compound by heating the potassium salt with bromine to 140° for sixteen hours, and also by heating it dissolved in strong sulphuric acid with bromine; but in neither case was hydrobromic acid given off, the trisulphonic acid remaining unaltered. It is possible, however, that longer heating with bromine might produce the desired result.

Our attempts to obtain a nitro acid were no more successful than those to make the bromine acid, as the potassic benzoltrisulphonate can be boiled with fuming nitric acid, or even with a mixture of fuming nitric acid and sulphuric acid, for over an hour without undergoing any alteration. When, however, the chloride is heated to 140° for sixteen hours with a large excess of fuming nitric acid, it is converted into a new substance with the most uninviting properties, which we have not studied further because sulphuric acid is eliminated in the process, and we propose to confine our attention to the trisulpho compounds.

Benzoltrisulphochloride, $C_6H_3(SO_2Cl)_3$.

This substance is prepared by heating the potassic benzoltrisulphonate, previously dried at 150°, with a little more than the calculated amount of phosphoric pentachloride (10 parts of the salt to 15 of the pentachloride) in a test-tube, or flask to 150° in an air-bath. If the substances are heated in a dish, there is little or no action. After the phosphoric oxychloride has distilled off, the product is treated with water, and finally warmed with it, but this warming should not be long continued, as the trisulphochloride is much more easily attacked by hot water than the benzolmetadisulphochloride. After washing the chloride thoroughly with warm water, it is purified by crystallization from boiling chloroform. The yield was between 80 and 90 per cent of the theoretical. Samples contaminated with lower sulphochlorides often can be freed from them by washing with ether. The substance dried at 100° gave the following results on analysis.

I. 0.2984 grm. gave after decomposition by boiling with a solution of potassic hydrate 0.3488 grm. of argentic chloride.

II. 0.1300 grm. treated in the same way gave 0.1530 grm. of argentic chloride.

III. 0.2374 grm. gave after decomposition with a boiling solution of pure sodic carbonate 0.2718 grm. of argentic chloride.

	Calculated for $C_6H_3(SO_2Cl)_3$.	Found. I.	II.	III.
Chlorine	28.52	28.90	29.10*	28.32

Properties. — The benzoltrisulphochloride crystallizes from chloroform in little silky flattened needles, which under the microscope are seen to have the ends bevelled, or occasionally terminated by two planes forming an obtuse angle; frequently groups are observed made up of a number of needles united longitudinally, giving a characteristic comb-like appearance to the ends. Out of benzol it forms good-sized plates, apparently belonging to the triclinic system. It melts at 184° (uncorr.), and sublimes with some difficulty at temperatures above 200°, forming good-sized flattened needles similar in shape to the crystals from benzol. It is insoluble in water, hot or cold, but is slowly decomposed and dissolved when boiled with it; very slightly soluble in cold alcohol, or methyl alcohol, but freely dissolved with decomposition when boiled with them, very slightly soluble in ligroine, slightly soluble in ether, freely in benzol, carbonic disulphide, glacial acetic acid, or chloroform. Chloroform is the best solvent for it, as it is much more soluble in it when hot than when cold. As already mentioned, the chloride is slowly converted into the acid by boiling water, and is much more easily attacked in this way than the benzolmetadisulphochloride, so that the acid can be prepared conveniently by heating it with water in open vessels, whereas with the di compound this reaction does not take place readily at temperatures below 140°. With boiling alcohol the product is also the acid; but this point will be discussed more fully under the ester. Solutions of potassic hydrate or carbonate, or a mixture of argentic oxide and water, when boiled with the chloride, convert it quickly and easily into the corresponding salt. The study of the action of reducing agents on the chloride will be reserved for a future paper.

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* The potassic hydrate used in I. and II. was not perfectly free from potassic chloride.

Benzoltrisulphonic Ester, $C_6H_3(SO_3C_2H_5)_3$.

This substance was prepared by the action of ethyliodide on argentic benzoltrisulphonate, made by boiling the chloride with argentic oxide, and, after filtering out the argentic chloride and excess of argentic oxide, evaporating to dryness on the water-bath, and drying at 100°. The ethyliodide acts on the silver salt with violence even in the cold, so that the process must be carried on in a flask with a return-condenser, and, after it has come to an end, which can be made sure by heating for a short time on the water-bath, the product is extracted with ether, and the extract purified by crystallization from benzol, and dried *in vacuo*. Ethylbromide may be used instead of ethyliodide, but in this case the mixture must be heated to 100° in a sealed tube to obtain complete action.

The ester can also be prepared by the action of benzoltrisulphochloride, mixed with a large excess of benzol, on the proper amount of sodic ethylate made from as little alcohol as possible; but this method is not so good as the preparation from the silver salt and ethyliodide. If the attempt is made to prepare the ester by the action of sodic ethylate dissolved in alcohol upon the benzoltrisulphochloride, the product is sodic benzoltrisulphonate, or, if absolute alcohol is substituted for sodic ethylate, benzoltrisulphonic acid, the ester at first formed being afterward decomposed by the absolute alcohol, according to the reaction given under the properties of the ester. The ester cannot be made by the action of hydrochloric acid gas on an alcoholic solution of the trisulphonic acid. The composition of the ester dried *in vacuo* was determined by the following analyses.

I. 0.2646 grm. of the substance gave by the method of Carius 0.4662 grm. of baric sulphate.

II. 0.156 grm. of the substance gave 0.2719 grm. of baric sulphate.

	Calculated for	Found.	
	$C_6H_3(SO_3C_2H_5)_3$.	I.	II.
Sulphur	23.88	24.16	23.94

Properties. — The benzoltrisulphonic ester forms well-developed shining white crystals, often more than a centimeter long, which belong to the triclinic system; a careful measurement of their angles was, however, impossible, because we could not obtain them with smooth enough faces. It melts at 147°, but if heated for some time to 110° is decomposed, leaving a residue of the benzoltrisulphonic acid; the reaction which takes place is probably the following,

$$C_6H_3(SO_3C_2H_5)_3 = C_6H_3(SO_3H)_3 + 3\ C_2H_4,$$

as 0.1674 grm. of substance lost 0.0324 grm.

Calculated for a loss of 3 C_2H_4.	Found.
20.89	19.36.

It is essentially insoluble in water, freely soluble in ether, chloroform, carbonic disulphide, or benzol, — the last being the best solvent for it, — insoluble in ligroine, decomposed and dissolved by glacial acetic acid, dissolves freely in alcohol, but is decomposed by it, as upon evaporating the solution, even if absolute alcohol is used, the benzoltrisulphonic acid is left. This reaction seemed to us so curious that we studied it more carefully, as follows. 10 grm. of benzoltrisulphochloride were boiled in a flask with a reverse cooler with 12 grm. of absolute alcohol; after half an hour the solid had completely dissolved, and upon examining the flask it was found that much hydrochloric acid had been formed, also apparently a little ethylchloride due to a secondary reaction, but no ethylene could be detected. The contents of the flask, after being freed from hydrochloric acid with potassic hydrate, were distilled fractionally with a Hempel's column, when it appeared that the principal product of the reaction was ethylether, recognized by its boiling-point, 35°, and by its smell. The following reactions, therefore, probably take place: —

$$\text{I.}\quad C_6H_3(SO_2Cl)_3 + 3\ C_2H_5OH = C_6H_3(SO_3C_2H_5)_3 + 3\ HCl;$$

$$\text{II.}\quad C_6H_3(SO_3C_2H_5)_3 + 3\ C_2H_5OH = C_6H_3(SO_3H)_3 + 3\ (C_2H_5)_2O;$$

and the action is exactly analogous to the ordinary method of making ethylether. Methylalcohol seems to act on the ester in the same way as ethylalcohol, — the residue left after evaporating a methylalcohol solution of it being benzoltrisulphonic acid. The ester was not acted on in the cold by sodium or sodic ethylate.

Benzoltrisulphamide, $C_6H_3(SO_2NH_2)_3$.

This substance was made by adding a very strong solution of ammonia to the benzoltrisulphochloride and allowing the mixture to stand a short time. It was purified by crystallization from boiling water. It can be formed also by the action of ammonic carbonate on the chloride, but the result was less satisfactory than with the solution of ammonia. The mother liquors from the crystallization contain a quantity of ammonic benzoltrisulphonate, which, after conversion into the potassium salt by boiling with potassic hydrate, can be reconverted into the chloride. The substance dried at 100° gave the following results on analysis.

I. 0.2358 grm. of substance gave after heating with soda-lime 0.1162 grm. of ammonic chloride.
II. 0.3739 grm. of substance gave according to the method of Carius 0.8318 grm. of baric sulphate.

	Calculated for $C_6H_3(SO_2NH_2)_3$.	Found.	
		I.	II.
Nitrogen	13.33	12.89	
Sulphur	30.47	. . .	30.56

Properties. — The benzoltrisulphamide crystallizes from boiling water in shining flattened needles with very sharp ends, sometimes nearly a centimeter long. It can also be obtained from water in square prisms with oblique ends, apparently of the monoclinic system, or in rhombic plates. From alcohol it crystallizes in long slender needles. Its melting point is 310°–315° (uncorr.); it is only slightly soluble in cold water, as shown by the following determination of its solubility.

I. 12.367 grm. of the solution saturated at 25° gave on evaporation 0.0172 grm. of the amide.
II. 11.164 grm. of the solution gave 0.0186 grm. of the amide.

The solution of the benzoltrisulphamide saturated at 25° contains, therefore,

I.	II.
0.14%	0.17%

It is much more freely soluble in boiling water than it is in cold, and this is the best solvent for it; soluble in alcohol, rather more so in methyl than in common alcohol; not very soluble in benzol; insoluble, or nearly so, in ether, ligroine, chloroform, or glacial acetic acid either hot or cold. The amide is much more soluble in a solution of ammonia than in water, but it is thrown down unaltered when the ammonia is driven off from such a solution by heat; it also dissolves very easily in a solution of potassic hydrate, and this solution is not decomposed, even when it is boiled for a short time. The hot aqueous solution of the amide gives a white precipitate with mercuric nitrate, but none with mercuric chloride; a difference in behavior which is not surprising when it is remembered how differently these two reagents act with acid sodic carbonate, sodic phosphate, oxalic acid, and even water. The composition of the precipitate formed with mercuric nitrate is discussed below. The hot solution of the amide also gives with mercurous nitrate a white precipitate, which becomes gray on standing, but no precipitate with solutions of the salts of any of the other common metals.

The *Silver Salt* $C_6H_3(SO_2NHAg)_3$ was made by adding argentic nitrate to a hot solution of the amide, and then ammonic hydrate, but not in excess, as this dissolves the precipitate; if by accident an excess has been added, the precipitate can be obtained again by boiling off the ammonia. The flocculent white precipitate thus formed was washed with water, dried *in vacuo*, and analyzed.

0.2778 grm. of the salt gave by precipitation from its solution in dilute nitric acid 0.1886 grm. of argentic chloride.

	Calculated for $C_6H_3(SO_2NHAg)_3$.	Found.
Silver	50.94	51.11

It is a tolerably stable white powder, insoluble in water, soluble in nitric acid or ammonic hydrate. When a little tincture of iodine is added, the silver is converted into argentic iodide. Compare the analogous reaction with the mercuric salt.

Mercuric Salts of Benzoltrisulphamide. — When the amide is boiled with yellow mercuric oxide suspended in water, a white precipitate is formed, the composition of which varies according to the proportion of oxide and amide used.

$C_6H_3(SO_2NHHgOH)_3$. — To prepare this salt, 0.65 grm. of mercuric chloride was converted into the oxide by precipitation with sodic hydrate, and the washed but not dried oxide boiled with a solution of 0.25 grm. of the amide. The action takes place very slowly even under these conditions (much more slowly and imperfectly if the oxide has been dried); but after boiling for twenty-four hours it was nearly complete, although there were still a few yellow specks of oxide visible. These were separated mechanically, as far as possible, and the precipitate washed and dried at 100°; its analysis is given under I. The same salt is obtained much more conveniently by adding a solution of mercuric nitrate to a boiling solution of the amide, and washing with boiling water. An analysis of the salt thus prepared, and dried at 100°, is given under II. It is probable that the mercuric nitrate forms at first the compound $C_6H_3(SO_2NHHgNO_3)_3$, and that this is decomposed by the hot water in the same way that mercuric nitrate itself is.

We do not pretend to determine, however, whether the hydroxyl is attached to the mercury or to the nitrogen, which in the latter case would be in the quinquivalent condition.

I. 0.299 grm. of substance dissolved in hydrochloric acid and treated with sulphuretted hydrogen gave 0.2164 grm. of mercuric sulphide.

II. 0.2756 grm. of substance gave 0.1994 grm. of mercuric sulphide.

	Calculated for $C_6H_3(SO_2NHHgOH)_3$.	Found. I.	Found. II.
Mercury	62.30	62.38	62.38

$[C_6H_3(SO_2NH)_3]_2Hg_3$. This salt was prepared like the preceding, by boiling the moist mercuric oxide from 0.65 grm. of mercuric chloride with 0.5 grm. of the amide in aqueous solution. Even greater difficulties were encountered than in the preceding case, the reaction taking place as slowly, and being less complete; on this account we have not succeeded in preparing the substance in a state of purity, as the following analysis shows; the difference is due to a slight excess of mercuric oxide, which could not be removed, but the result is near enough to leave no doubt about the formula of the compound.

0.3416 grm. of substance dried at 100° gave 0.2056 grm. of mercuric sulphide.

	Calculated for $[C_6H_3(SO_2NH)_3]_2Hg_3$.	Found
Mercury	49.02	51.88

Both substances are white powders, insoluble in water, soluble in hydrochloric acid, which form mercuric iodide when boiled with water and iodine for some time; the filtrate, however, contains no organic substance except unaltered benzoltrisulphamide.

The aqueous solution of the amide boiled with plumbic oxide formed white flocks, but the action took place with so much difficulty that we did not try to prepare the substance for analysis. With cupric oxide we could observe no action. A solution of the sulphate of cuprammonium took up the amide with great avidity, forming a dark blue solution, which deposited azure blue disks of so deep a tint as to look nearly black, while the mother liquor showed only a very pale blue color. The solid was but sparingly soluble in water, being decomposed by it, but tolerably stable in the dry state; dissolved in dilute hydrochloric acid, it gave no precipitate with baric chloride. It was dried in a desiccator, and its composition determined by the following analyses.

I. 0.1628 grm. of substance dissolved in hydrochloric acid and precipitated with sodic hydrate gave 0.0356 grm. of cupric oxide.

II. 0.2564 grm. gave 0.0596 grm. of cupric oxide.

	Calculated for $[Cu(NH_3)_4]_3[(SO_3)_3C_6H_3]_2$.	Found.	
		I.	II.
Copper	18.57	17.46	18.57

No better agreement between these results could be expected, when it is remembered that the substance could not be recrystallized. It is evidently cuprammonic benzoltrisulphonate, but we were unable to prepare it by the action of cuprammonic sulphate on a solution of potassic benzoltrisulphonate.

Several attempts to obtain the *imide* $[C_6H_3(SO_2)_3]_2(NH)_3$, although they led to no definite results, may be mentioned here. The benzoltrisulphochloride mixed with absolutely dry benzol and the silver salt of benzoltrisulphamide, and heated to 100° in a sealed tube for two days, remained entirely unaltered. The experiment could not be repeated at a higher temperature for fear of decomposing the silver salt. If the chloride was heated with the amide, in the proportion of one molecule of each, to 190°, there was no action; but if the temperature was raised to 200°–210°, and maintained at this point for some hours, hydrochloric acid was given off, and a black product formed, which, when treated with cold water, swelled up to a gelatinous mass, the water becoming acid with hydrochloric acid. The jelly thus obtained, after being thoroughly washed with water, dried to a more or less colored powder, insoluble in all the solvents that we have tried, so that we have not been able to purify it properly for analysis. Some nitrogen determinations made with a substance extracted with all the common solvents gave results not far removed from the numbers required by the imide; but they are entitled to little, if any, confidence, as the substance still contained some chlorine. We satisfied ourselves by a special experiment that the substance mentioned above was not formed from the benzoltrisulphamide alone, since the amide was not altered by heating it to a temperature of 230° for an hour and a half.

Benzoylbenzoltrisulphamide, $C_6H_3(SO_2NHCOC_6H_5)_3$.

Benzoylchloride has no action on benzoltrisulphamide when the two substances are heated together on the water-bath; if, however, the mixture of these substances in the proportion of three molecules of the chloride to one of the amide (1.3 grm. to 1 grm.) is heated in a flask with a return-cooler to 140° by means of an oil-bath, hydrochloric acid is given off, and the benzoyl derivative is formed. During the process great care must be taken that the temperature does not rise above 150°, as at a point but little above this (150°–180°) decomposition sets in, and in that case the principal product of the action is kyaphenine. After the action has come to an end, which usually takes from five to seven hours, the product is extracted with benzol to remove any undecomposed benzoylchloride, and purified by crystallization from hot alcohol. Dried at 100° it gave the following results on analysis.

I. 0.2234 grm. of substance gave 13.3 c.c. of nitrogen under a pressure of 766 mm., and at a temperature of 22°.

II. 0.1632 grm. of substance gave by the method of Carius 0.1784 grm. of baric sulphate.

	Calculated for $C_6H_3(SO_2NHC_7H_5O)_3$.	Found. I.	Found. II.
Nitrogen	6.69	6.79	
Sulphur	15.31	. . .	15.02

Properties. — The benzoylbenzoltrisulphamide crystallizes from alcohol in rather short and stout well-formed prisms, with an unmodified basal plane, which seem to belong to the hexagonal system. It has no definite melting point, since it decomposes at comparatively low temperatures (below 200°), and the melting point is therefore modified by the length of time during which the substance has been heated. The highest point which we have observed is 285°, but this can be materially modified by altering the conditions under which the melting point is taken; for instance, two tubes were filled with portions of the same preparation, and one of them was allowed to hang in the bath in the usual way, when it melted at 264°, while the other, which was not allowed to remain in the bath, but only dipped into it occasionally, did not melt till 275°. The two observations were made at the same time, so that in all other respects the conditions were the same. The melting is accompanied with blackening and effervescence. By long continued heat at temperatures between 150° and 180°, the substance is completely decomposed, giving kyaphenine as the principal product, which was recognized by its melting point, 230° (Pinner and Klein * give 231°). The decomposition is undoubtedly similar to that of the corresponding mono compound, which, according to Wallach and Gossmann,* gives kyaphenine or benzonitrile and benzolmonosulphonic acid. The benzoyl compound is nearly insoluble in water, whether hot or cold, but not absolutely so, as a moist crystal, after being boiled with water, if laid upon litmus paper, gives an acid reaction. It is tolerably soluble in alcohol or methylalcohol, especially when boiling, nearly insoluble in ether, chloroform, or glacial acetic acid, essentially insoluble in ligroine, benzol, or carbonic disulphide. It is easily soluble in sodic, ammonic, or baric hydrates, or in sodic carbonate; hydrochloric acid precipitates the original substance from these solutions. The solution in ammonic hydrate, if evaporated to dryness on the water-bath, leaves a colorless varnish, which dissolves again in water; this solution, however, gives no characteristic precipitates with the common reagents, although we may mention the white precipitates produced by argentic nitrate and basic plumbic acetate (neutral plumbic acetate gives no precipitate). We have studied the sodium and barium salts, and intended also to analyze the silver salt, but found that it was too soluble to be purified conveniently by washing, and came down from its hot aqueous solution as a varnish.

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* Ber. d. ch. G., 1878, p. 764.

Sodic Benzoylbenzoltrisulphamide, $C_6H_3(SO_2NNaC_7H_5O)_3$. — This salt was made by boiling a solution of the calculated amount of sodic carbonate with benzoylbenzoltrisulphamide, and evaporating to dryness, finally spontaneously. Upon drying at 100° it lost varying amounts of water, but in no case so much as one molecule; we are therefore inclined to think it was only hygroscopic water, as the salt was of a varnish-like consistency, which would offer great resistance to air-drying.

0.2466 grm. of the salt dried at 100° gave 0.0794 grm. of sodic sulphate.

	Calculated for $C_6H_3(SO_2NNaC_7H_5O)_3$.	Found.
Sodium	9.95	10.43

The salt is a white varnish, which we did not succeed in obtaining in crystals; it dissolves in water very slowly, but does not need a large amount for complete solution. The solution is neutral, and we did not succeed in preparing an acid salt, as when the free benzoylbenzoltrisulphamide was boiled with one molecule of sodic carbonate, nearly two thirds of the amide remained undissolved, and the solution was barely acid.

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* Ber. d. ch. G., 1878, p. 754.

Baric Benzoylbenzoltrisulphamide, $[C_6H_3(SO_2NC_7H_5O)_3]_2Ba_3 12 H_2O$. — This salt was made by boiling the benzoylbenzoltrisulphamide with a solution of baric hydrate, and removing the excess of baric hydrate with carbonic dioxide. The solution was evaporated at last spontaneously.

I. 0.3192 grm. of the air-dried salt dried at 100° lost 0.0372 grm.
II. 0.3406 grm. at 120° lost 0.0408 grm.

	Calculated for $[C_6H_3(SO_2NC_7H_5O)_3]_2Ba_3 12 H_2O$.	Found. I.	 II.
Water	11.53	11.65	11.97

The air-dried salt loses *in vacuo* 3.66 per cent, which corresponds to 3½ molecules of water (calculated 3.36 per cent).

I. 0.2820 grm. of the dry salt gave 0.1184 grm. of baric sulphate.
II. 0.2998 grm. gave 0.1214 grm. of baric sulphate.

	Calculated for $[C_6H_3(SO_2NC_7H_5O)_3]_2Ba_3$.	Found. I.	 II.
Barium	24.77	24.69	23.80

It forms a white varnish soluble in water.

Chloride of Benzoylbenzoltrisulphamide, $C_6H_3(SO_2N{=}CClC_6H_5)_3$.

This substance was made by heating the benzoylbenzoltrisulphamide with phosphoric pentachloride. Equal weights of the two substances were used, and they were heated in an open test-tube by means of an air-bath at 110°. After one hour the reaction was complete, and the product was purified by washing it with ligroine, and afterward with absolute ether, which converts it from a viscous liquid to a powder. It was dried at 100° and analyzed.

I. 0.2314 grm. of substance gave, after boiling with a solution of pure sodic carbonate, 0.1514 grm. of argentic chloride.
II. 0.2502 grm. of substance gave 0.1614 grm. of argentic chloride.

	Calculated for $C_6H_3(SO_2NCClC_6H_5)_3$.	Found. I.	 II.
Chlorine	15.61	16.17	15.95

Properties. — It forms colorless cubic crystals, which, like the benzoyl compound from which they are derived, show no definite melting point; they begin to decompose at 225°, and become liquid in the neighborhood of 245°, but the melting point may vary as much as 30°. The substance is insoluble in water, benzol, ligroine, and chloroform, somewhat soluble in ether.

Benzoltrisulphobenzenylphenylamidine, $C_6H_3[SO_2N{:}C(NHC_6H_5)C_6H_5]_3$.

The chloride just described was converted by warming it gently with aniline into a viscous mass, which solidified after long standing. The substance was purified by washing with water, ether, and benzol, and then crystallizing from hot alcohol until it showed a constant melting point. It was then dried at 100°, and analyzed.

0.1658 grm. of substance gave 14.1 c.c. of nitrogen at a pressure of 760 mm., and a temperature of 20°.

	Calculated for $C_6H_3(SO_2N_2C_{13}H_{11})_3$.	Found.
Nitrogen	9.86	9.73

Properties. — It forms white needles, which melt at 196° (uncorr.), and are insoluble in water and ligroine, soluble with difficulty in alcohol, which, however, is the best solvent for it, soluble in ether, benzol, and chloroform.

A number of attempts to make the dibenzoylbenzoltrisulphamide $C_6H_3[SO_2N(C_7H_5O)_2]_3$ led to no result. The substance was not formed when the sulphamide was heated to 140° with six molecules of benzoylchloride instead of three, or when the sodium salt of the benzoylbenzoltrisulphamide was heated to 150° for a day with an excess of benzoylchloride, or when the silver salt of the benzoylbenzolsulphamide (made by adding argentic nitrate to the sodium salt) was heated to 100° in a sealed tube with an excess of benzoylchloride. In every case the monobenzoylbenzoltrisulphamide remained unaltered.

Benzoltrisulphanilid, $C_6H_3(SO_2NHC_6H_5)_3$.

This substance was prepared by warming benzoltrisulphochloride with aniline. The product was boiled out with water, and purified by crystallization from alcohol. Dried at 100°, it gave the following result on analysis.

0.2408 grm. of the substance gave, according to the method of Carius, 0.315 grm. of baric sulphate.

	Calculated for $C_6H_3(SO_2NHC_6H_5)_3$.	Found.
Sulphur	17.68	17.97

Properties. — It forms good-sized short, thick, white prisms, which melt at 237°, and are very slightly soluble in boiling water, soluble in alcohol, ether, benzol, or acetone, but insoluble in ligroine.

Constitution of Benzoltrisulphonic Acid.

We have determined the constitution of the acid in the two following ways.

First Method. — Dry potassic benzoltrisulphonate was mixed thoroughly with exactly the theoretical amount of potassic cyanide (1 grm. to 0.45 grm.), — if an excess of the cyanide is used, the yield is very much diminished, — and heated by means of a gas-furnace in a piece of combustion-tubing closed at one end; the white crystalline sublimate which collects in the cold part of the tube was removed, and saponified by boiling with alcoholic potassic hydrate, a process which lasts several days. When the evolution of ammonia ceased, the contents of the flask were acidified with hydrochloric acid, and shaken with ether; the ether extract was an acid which melted at 320°–325°, and this melting point remained unaltered after crystallization from water. It was converted into the silver salt, which gave the following result on analysis.

0.1528 grm. of the salt gave on ignition 0.093 grm. of metallic silver.

	Calculated for $C_6H_3(CO_2Ag)_3$.	Found.
Silver	61.02	60.86

No other acid could be detected in the product of the reaction. The melting points of the three tribasic acids derived from benzol are, hemimellitic acid, 185°; trimellitic acid, 216°; trimesic acid, above 300°. So there can be no doubt that our acid is *trimesic acid*, and therefore, if there has been no intramolecular transformation, the benzoltrisulphonic acid has the symmetrical constitution 1, 3, 5.

Second Method. — The benzoltrisulphochloride was heated with an excess of phosphoric pentachloride, according to the method of Barbaglia and Kekulé[*] for replacing a sulpho-group by an atom of chlorine. For this purpose 3 grm. of the chloride were sealed with 5.2 grm. of phosphoric pentachloride (one molecule of the sulphochloride to six of the phosphoric pentachloride), and heated for some hours to 200°–210°. Upon treating the product with water long needles were deposited, which were purified by washing with sodic hydrate, and several crystallizations from alcohol, when they melted at 63°. The yield was about 62 per cent of the theoretical. The melting point of this substance would indicate that it is the symmetrical trichlorbenzol 1, 3, 5, which melts, according to Beilstein and

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[*] Ber. d. ch. G., 1872, p. 875.

Kurbatow,* at 63°.5. To confirm this indication we treated a portion of the substance with fuming nitric acid at a temperature of about 50°, when, instead of getting the trichlormononitrobenzol of Beilstein and Kurbatow,† melting at 68°, we obtained a substance crystallizing in long, thick prisms, and melting at 130°. This observation made it necessary for us to study the action of fuming nitric acid on symmetrical trichlorbenzol, the results of which research are described fully in the following paper. It is sufficient to state here, that we found the nitric acid used by us, even when acting in the cold, converted the symmetrical trichlorbenzol into the trichlordinitrobenzol, melting at 129°.5, thus proving that the trichlorbenzol derived from benzoltrisulphochloride is the symmetrical compound (1, 3, 5), and confirming the result obtained by the first method.

The study of the action of reducing agents on the benzoltrisulphochloride will be described in a subsequent paper, and Mr. G. T. Hartshorn has undertaken the extension of this method of making sulpho acids to other organic substances, obtaining results which will soon be ready for publication.

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* Ann. Chem., cxcii. 233.

† Ber. d. ch. G., 1877, p. 271.